Proceedings of the Iowa Academy of Science

Volume 17 | Annual Issue Article 16

1910

# A Study in the Determination of Calcium

George Heise

# A STUDY IN THE DETERMINATION OF CALCIUM.

BY GEORGE HEISE.

In this series of experiments it has been attempted to simplify the gravimetric determination of calcium, to make it a more satisfactory and convenient laboratory method.

The precipitation of calcium as the oxalate and its subsequent conversion by heating to the oxide is a method which presents some difficulties, especially to the inexperienced student. To entirely convert all the calcium to the oxide is a long and tedious process at best, besides, especially when porcelain crucibles are used, it is almost impossible to heat the oxide down to constant weight.

It occurred to us that it might be feasible to precipitate calcium as the oxalate in the usual manner, to filter it through a Gooch crucible, to weigh it directly as the oxalate, or to change the oxalate to the carbonate by careful heating, and to weigh as the carbonate.

A careful search through the literature revealed only one article* in which the conversion of the oxalate into the carbonate by heating is recommended as a method for the gravimetric determination of calcium (Strentium, Barium). The heating was done in a capped Gooch crucible over a free Bunsen flame. No precautions or special directions were given and the results, though fairly accurate, were low in each case, showing the partial decomposition of the carbonate into the oxide.

It shall be my endeavor to show how calcium may be determined directly as the oxalate in a Gooch crucible and how the oxalate may be converted into the carbonate by heating without danger of loss by decomposition.

A carefully weighed amount of the purest obtainable calcite was introduced into a graduated litre flask, covered with dilute HCL and allowed to decompose. The flask was then filled to the mark with water. The solution, which was perfectly clear and free from residue, was kept in a glass-stoppeed bottle and convenient quantities for analysis were withdrawn as needed by means of a graduated pipette.

*Estimation of Calcium, Strontium and Barium as the Oxalates (with KMNO). Am. Jour. Sci. Series 4-I. (1901) 216.

The precipitation of calcium was performed in accordance with the method described by T. W. Richards.* Oxalic acid was added to the hot, acid solution of calcium chloride, the solution was then made just alkaline by the slow addition of ammonia, methyl orange being used as an indicator, finally excess of ammonium oxalate was added and the precipitate was allowed to stand about four hours.

Ordinary glazed porcelain Gooch crucibles with porcelain plates and asbestos mats were used for filtration. Calcium oxalate filters somewhat slowly but the filtrate comes through perfectly clear. The precipitates were washed with a dilute solution of ammonium oxalate, finally with a little water.

Calcium oxalate precipitates with either one or three molecules of water of crystallization, and gives up this water at 205 degrees centigrade. Heating the oxalate for from thirty to forty-five minutes in a drying oven at a temperature of 225-250 degrees was found sufficient to dehydrate it completely. It behaves very much like the oxide, taking up moisture from the air very readily. It is necessary to heat, weigh, reheat for ten minutes, dessicate a second time and reweigh rapidly to get the correct weight. It is generally possible to get within one or two milligrams of the correct weight at the first trial. The results obtained show that it is practicable to determine calcium quickly and accurately as the oxalate. In heating, I found that the oxalate would not decompose though it was heated for an hour at 340 degrees.

As will be seen from the first table (below), the results are well within the limits of experimental error. However, to confirm the results obtained or to find the error, if any, it was thought wise to weigh also as carbonate, if some surer method of converting the oxalate could be devised. Determinations 1 and 2 were heated over a low Bunsen flame without any special precautions, dessicated and weighed. In subsequent determinations, the crucibles were heated high over a moderately large Bunsen flame to incipient redness and fairly accurate resutls were obtained.

A table showing the results of the first series of determinations follows:

*Ztschr. fuer Anorg. Chemie, 28-170-(1901).

TABLE I.

DETERMINATIONS IN PORCELAIN GOOCH CRUCIBLES.

| Number | Weight of Oxalate | Calculated Weight | Error | Weight of Carbonate | Calculated Weight | Error |
|---|---|---|---|---|---|---|
| 1 | 0.4870 g | 0.4867 g | +.0003 g | 0.3850 g | 0.3802 g | +.0048 g |
| 2 | .4870 g | .4867 g | +.0003 g | .3830 g | .3802 g | +.0028 g |
| 3 | .4875 g | .4867 g | +.0008 g | .3818 g | .3802 g | +.0016 g |
| 4 | .4870 g | .4867 g | +.0003 g | .3816 g | .3802 g | +.0014 g |
| 5 | .1942 g | .1947 g | —.0005 g | .1510 g | .15209 g | —.0011 g |
| 6 | --------- | .1947 g | --------- | .1526 g | .15209 g | +.0005 g |

Note.—Calculations are based on weight of calcite.

The first preliminary determinations having succeeded so well, the second series was begun, this time in a platinum Gooch, to make possible the weighing of calcium not only as the oxalate and carbonate, but also as the oxide. Thus a double check on the accuracy of the work could be secured. In this series it was likewise attempted to devise a clean-cut and efficient method of converting the oxalate into the carbonate, without necessitating the weighing as oxide to check results. Most teachers would hesitate to advocate weighing of calcium as the carbonate unless more certain and specific directions for the conversion of the oxalate could be laid down.

The oxalate was precipitated in the usual manner and weighed in a covered Platinum Gooch crucible. For the conversion to the carbonate the following scheme was devised:

The Gooch crucible was placed on a thin piece of asbestos in a large iron crucible. The iron crucible was then covered with a porcelain cover and heated to the highest possible temperature over a full Bunsen flame.

The results obtained were as accurate as could be wished for. Heating by this method for 20-30 minutes brought the carbonate down to constant weight and eliminated all danger of decomposition by superheating.

As an added check the carbonate was converted to the oxide in a blast lamp, using a capped platinum Gooch, yielding results concordant with the calculated value in each case.

The second series follows:

TABLE II.

DETERMINATIONS IN PLATINUM GOOCH.

| Number | Weight of Oxalate | Calculated Weight | Error | Weight of Carbonate | Weight of Oxide | Calculated Weight | Error |
|---|---|---|---|---|---|---|---|
| 8 | 0.3912 g | 0.3911 g | +.0001 g | 0.3056 g | 0.1710 g | 0.1711 g | —.0001 g |
| 9 | 0.3945 g | .3938 g | +.0007 g | .3076 g | .1722 g | .1722 g | .0000 |
| 10 | .3916 g | .3913 g | +.0003 g | .3058 g | .1716 g | .1713 g | +.0003 |
| 11 | .8666 g | .8666 g | .0000 g | .6770 g | .3794 g | .3791 g | +.0003 |
| 12 | .8820 g | .8819 g | +.0001 g | .6890 g | .3858 g | .3858 g | .0000 |

Note.—Calculated weights based on weights of carbonates.

The results of these experiments may be briefly summarized as follows:

Calcium can be determined and accurately weighed as the oxalate.

It can be very conveniently converted into the carbonate and weighed as such.

The determinations can be carried out in porcelain crucibles without appreciable error.

Either of the above mentioned methods is fully as accurate as the determination of calcium as the oxide and is much more convenient and rapid.

Of the two methods, the determination as carbonate is somewhat superior to the determination as oxalate, because of the hydroscopic nature of the latter substance.

I wish at this time to express my thanks to Professor W. S. Hendrixson for his suggestions and help in the working up of this series of experiments.